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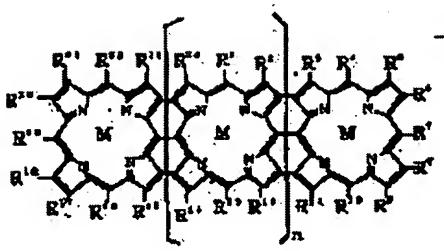
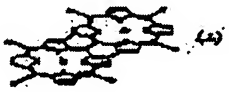
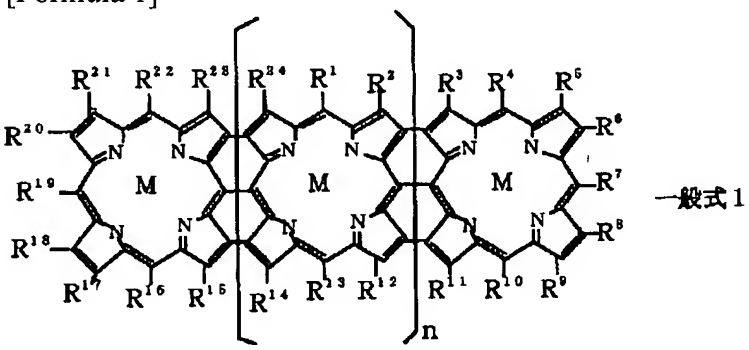
(54) **PORPHYRIN COMPOUND WHOSE PORPHYRIN RINGS ARE FUSED TO EACH OTHER IN ONE DIRECTION WITH THREE BONDINGS OF MESO-MESO CARBON BOND AND TWO B-B CARBON BONDS, AND METHOD FOR SYNTHESIZING THE SAME**





(57)Abstract:
PROBLEM TO BE SOLVED: To provide a porphyrin compound derivative having a structure capable of improving expanded π-electron network and the length of electron delocalization.
SOLUTION: A ring-fused porphyrin multimer formed by directly binding porphyrin rings expressed by general formula I with three covalent bonds, that is, one covalent bond between a meso-position and a meso-position, and two pairs of covalent bonds between β-position and β-position which adjacent to the meso-position. Concrete examples of the ring-fused porphyrin multimer include the compound of formula 2. Further, a compound 1 is synthesized by performing the ring condensation of the corresponding compound 3 in the presence of a Lewis acid comprising quinoline and a rare earth.

[Claim(s)]
[Claim 1] The condensed ring porphyrin polymer to which the porphyrin ring expressed with a general formula 1 coupled at least the beta directly with the beta by three covalent bond like a beta with two betas by which at least mezzo-soprano adjoins this with mezzo-soprano.
[Formula 1]



一般式1

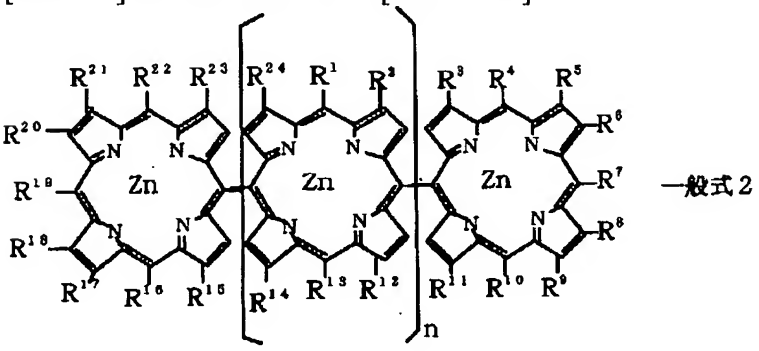
here -- R1-R24 -- respectively -- independent -- hydrogen, a halogen, and a hydroxyl group -- A sulfhydryl group, the amino group, a nitro group, a cyano group, a carboxyl group, a sulfonic group, The alkoxy group which is not permuted [the aryl group which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or], The alkylthio group which is not permuted [the aryloxy group which is not permuted / a permutation or /, a permutation, or], The arylamino radical which is not permuted [the aryl thio radical which is not permuted / a permutation or / an alkylamino radical, a permutation, or], The carboxylic-acid amide group which is not permuted [the carboxylate radical which is not permuted / a

permutation or /, a permutation, or], The sulfonamide radical which is not permuted [the sulfonate radical which is not permuted / a permutation or /, a permutation, or], It is chosen from the siloxy radical which is not permuted [the silyl radical which is not permuted / the carbonyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or]. The group of the metal atom of complex M. with which n replaced the metal atom with which two hydrogen atoms, the porphyrin of the metal free-lancer who are one or more integers, or NH radical in a porphyrin ring, are chosen from one or more metal atom groups of following M. Zn, Mg, calcium, Sr, Ba, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, They are Zr, Hf, V, Nb, Ta, Th, U, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, Pt, Cu, Ag, Au, Cd, Hg, aluminum, Ga, In, Tl, Si, germanium, Sn, Pb, As, Sb, and Bi.

[Claim 2] a general formula 1 -- setting -- R1 and R -- 4, R10, R13, R16, and R22 it chooses independently of the phenyl group which has the substituent chosen independently of a phenyl group, a with a carbon numbers of one or more alkyl group, or an alkoxy group -- having -- R7 and R19 Independently, respectively Hydrogen, a halogen, a hydroxyl group, a sulfhydryl group, the amino group, The alkyl group which is not permuted [a nitro group, a cyano group, a carboxyl group, a sulfonic group a permutation, or], The alkoxy group which is not permuted [the aryl group which is not permuted / a permutation or /, a permutation, or], The alkylthio group which is not permuted [the aryloxy group which is not permuted / a permutation or /, a permutation, or], The arylamino radical which is not permuted [the aryl thio radical which is not permuted / a permutation or / an alkylamino radical, a permutation, or], The carboxylic-acid amide group which is not permuted [the carboxylate radical which is not permuted / a permutation or /, a permutation, or], The condensed ring porphyrin compound according to claim 1 characterized by being the siloxy radical which is not permuted [the silyl radical which is not permuted / the carbonyl group which is not permuted / the sulfonamide radical which is not permuted / the sulfonate radical which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or].

[Claim 3] The condensed ring porphyrin compound according to claim 1 or 2 characterized by choosing R1, R4, R10, R13, R16, and R22 in a general formula 1 independently of 3, 5-G TASHARU buthylphenyl radical or 3, and 5-G octyloxy phenyl group.

[Claim 4] General formula 2 [Formula 2]



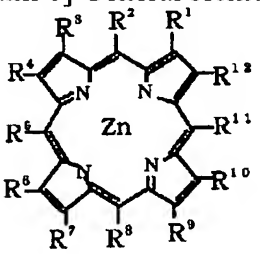
一般式2

(However if R1-R24 can be set to a general formula 1 the same semantics.) The porphyrin ring which 0 or the ZnII-porphyrin of one or more integers is made to

condense the ring in the solvent with which the quinone and rare-earth-elements **** Lewis acid which are an oxidizer exist, and adjoins each other combines n mutually with the carbon like each mezzo-soprano. In said general formula 1 to which the porphyrin ring which adjoins each other by a total of three association of two beta-beta carbon to carbon bonds by the carbon like two beta by which at least the mezzo-soprano adjoins carbon joining together mutually has extended in the one direction n And 0 or one or more integers, The condensed ring metal free porphyrin compound or condensed ring M+n-porphyrin compound to which M carried out coordination of demetallization or other metals for Zn of the condensed ring ZnII-porphyrin compound of Zn, and this condensed ring ZnII-porphyrin compound It is the manufacture approach of (the ionic valence [however,] to which M is a metal chosen from the group of said metal atoms other than Zn, and each metal can take n).

[Claim 5] In a general formula 2 R1, R4, R7, R10, R13, R16, R19, and R22 A phenyl group, Or the condensed ring ZnII-porphyrin compound according to claim 4 characterized by being the phenyl group permuted by the substituent chosen independently of a with a carbon numbers of one or more alkyl group or an alkoxy group, And the condensed ring metal free porphyrin compound or condensed ring M+n-porphyrin compound to which coordination of demetallization or other metals was carried out for Zn of this condensed ring ZnII-porphyrin compound (-- however, the metal with which M is chosen from the group of said metal atoms other than Zn -- it is -- n -- the manufacture approach of ****** ionic valence) of each metal.

[Claim 6] General formula 3 [Formula 3]



一般式3

R10-R12 -- hydrogen, and R1-R9 -- respectively -- independent -- hydrogen -- [however,] A halogen, a hydroxyl group, a sulfhydryl group, the amino group, a nitro group, a cyano group, The aryl group which is not permuted [the alkyl group which is not permuted / a carboxyl group, a sulfonic group, a permutation, or /, a permutation, or], The aryloxy group which is not permuted [the alkoxy group which is not permuted / a permutation or /, a permutation, or], The aryl thio radical which is not permuted [the alkylthio group which is not permuted / a permutation or /, a permutation or], The carboxylate radical which is not permuted [the arylamino radical which is not permuted / an alkylamino radical, a permutation, or /, a permutation, or], The sulfonate radical which is not permuted [the carboxylic-acid amide group which is not permuted / a permutation or /, a permutation, or], The carbonyl group which is not permuted [the sulfonamide radical which is not permuted / a permutation or / a permutation, or], The ZnII-porphyrin of the siloxy radical which is not permuted [the silyl radical which is not permuted / a permutation or /, a permutation, or] Make it condense the ring in the solvent with which the Lewis acid containing the quinone and rare earth elements which are oxidizers exists, and two porphyrin rings join together mutually with the carbon like each mezzo-soprano. By and a total of three association of two beta-beta carbon to carbon

bonds by the carbon like two beta by which at least the mezzo-soprano adjoins carbon joining together mutually The condensed ring metal free porphyrin compound to which coordination of demetallization or other metals was carried out for Zn of the condensed ring ZnII-porphyrin compound with which the adjacent porphyrin ring is prolonged in the one direction, and this condensed ring ZnII-porphyrin compound, or a condensed ring M+n-porphyrin compound (however) It is the manufacture approach of an ionic valence that M is a metal chosen from the group of the aforementioned metal atoms other than Zn, and each metal can take n.

[Claim 7] R1, R3, R4, R6, R7, R9-R12 of a general formula 3 -- hydrogen, R2, R5, and R8 Two porphyrin rings according to claim 6 characterized by using the ZnII-porphyrin which is the phenyl group which has the substituent chosen independently of a phenyl group, a with a carbon numbers of one or more alkyl group, or an alkoxy group join together mutually with the carbon like each mezzo-soprano. And two beta-beta carbon to carbon bonds by the carbon like two beta by which at least the mezzo-soprano adjoins carbon joining together mutually, By a total of three association The condensed ring metal free porphyrin compound to which coordination of demetallization or other metals was carried out for Zn of the condensed ring ZnII-porphyrin compound with which the adjacent porphyrin ring is prolonged in the one direction, and this condensed ring ZnII-porphyrin compound, or a condensed ring M+n-porphyrin compound (however) It is the manufacture approach of an ionic valence that M is a metal chosen from the group of the aforementioned metal atoms other than Zn, and each metal can take n.

[Claim 8] The condensed ring ZnII-porphyrin compound according to claim 5 or 7 characterized by the phenyl group permuted by the substituent chosen independently of a with a carbon numbers of one or more alkyl group or an alkoxy group being a phenyl group which permuted TASHARU butyl or an OKUCHIRUOKI radical by the 3 or 5th place, The manufacture approach of the condensed ring metal free porphyrin compound to which coordination of demetallization or other metals was carried out for this Zn, or a condensed ring M+n-porphyrin compound (however, ionic valence to which M is a metal chosen from the group of the aforementioned metal atoms other than Zn, and each metal can take n).

[Claim 9] By three association with two beta-beta carbon to carbon bonds which the carbon like two beta next to the carbon like the mezzo-soprano-mezzo-soprano carbon to carbon bond which two or more porphyrin rings combine mutually with the carbon like each mezzo-soprano, and said mezzo-soprano combines mutually The aromatic hydrocarbon solvent with which the Lewis acid containing the element of the oxidizer chosen from quinones in the chemical reaction which obtains the compound with which the adjacent porphyrin ring condensed the ring, and rare earth exists is used. The manufacture approach of the condensed ring metal free porphyrin compound according to claim 4 to 8 characterized by making it go on under reflux, or a condensed ring M+n-porphyrin compound (however, ionic valence to which M is a metal chosen from the group of the aforementioned metal atom, and each metal can take n).

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]

[Field of the Invention] This invention so that higher smoothness and bigger electronic conjugate property may be held the condensed ring porphyrin compound with which four or more porphyrin rings condensed the ring -- especially Un-permuting by or the phenyl group which has a substituent in the 3 or 5th place [R1-R9 which are expressed with the condensed ring porphyrin compound and the (1) general formula 3 to which the porphyrin ring condensed the ring mutually to the one direction by association of three, especially R2, R5 and R8] The oligo or the Pori (mezzo-soprano-mezzo-soprano joint porphyrin) compound with which two or more ZnII-porphyrin rings, the ZnII-porphyrin permuted or the (2) general formula 3, joined together the carbon like mezzo-soprano mutually, and are prolonged in the one direction It is related with the approach of manufacturing the condensed ring porphyrin compound with which the porphyrin ring which is made reacting in the solvent carried out under existence of the oxidizer chosen from quinones and the Lewis acid containing rare earth elements, and is expressed with a general formula 1 condensed the ring.
[0002]

[Description of the Prior Art] Since strong absorption and strong fluorescence, and a phosphorescence luminescence property are remarkable and the HOMO-LUMO gap is small, the porphyrin molecule has the high property of electrical conductivity. Moreover, almost all metallic elements can be incorporated to a central hole as a ligand, and it has the versatility which adjustment of optical physical properties or a oxidation reduction property is possible, and can meet the demand as a broad functional material with the incorporated metal. Porphyrins are bearing various functions, such as an electron transport component, also in in the living body in living body processes, such as the oxidation reduction catalyst operation and photosynthesis in a metabolic turnover, and breathing. Paying attention to these functions, development as an ingredient with an energy conversion function or a living body mold oxidation reduction catalyst is being performed. Although many researches which use a porphyrin polymer as a photoelectron ingredient and improve it are done recently, there is much research which observed that the polymer and oligomer of stiffness and the Takayasu quality structure can be made and the strong light absorption and the strong fluorescence in a light field, phosphorescence luminescence, a small HOMO-LUMO energy gap, etc. as a block unit in which a porphyrin molecule assembles long pi conjugated-system structure.
[0003] Thus, this invention person also makes a porphyrin molecule a block unit. Oligomer and the polymer from a porphyrin molecule which carried out a maximum of 300 to 400 unit association in the one direction by association (MEZOMEZO carbon to carbon bond) of the carbon like each mezzo-soprano of this porphyrin molecule, And the condensed ring object of the porphyrin unit combined in the die-length direction which at least the mezzo-soprano of the molecule of another side, on the other hand, combined [direction] each of the carbon like beta of a molecule and the carbon like mezzo-soprano with the carbon like beta, namely, combined this porphyrin molecule by two association of beta-mezzo-soprano and mezzo-soprano-beta etc. has been proposed. And it has been expected as a promising photon wire, a molecule wire, etc. from have the dominance

description that no energy sink (sink) which blocks transfer of the energy with which this mezzo-soprano-mezzo-soprano joint porphyrin array compound had sufficient electronic interaction to start those cylindrical configurations that it has, and enough and quick uncoherent energy hopping, and met the array is. These properties are properties resulting from the gestalt with the inclination which makes the electronic interaction between adjacent porphyrins min which intersects perpendicularly, and when an array is formed in a plane and is conjugating more electronically, they can constitute the conductive molecule wire of a practical molecule scale. A MEZOMEZO joint porphyrin array is because isolated 128 **** of about 108nm of molecule length have already been obtained.

[0004] However, it cannot be said that they have still more sufficient property as a conductive wire etc. since said MEZOMEZO joint porphyrin arrays are not what porphyrins combined by two direct coupling (it is called a double bond or a condensed ring.), and the thing of the structure which constitutes the pi electron-network expanded in common if it puts in another way. Then, this invention person is said mezzo-soprano further. - By two association of beta and beta-mezzo-soprano, the condensed ring object of the porphyrin compound which made the porphyrin unit extend in the die-length direction, i.e., a porphyrin compound, was proposed, and the more practical compound as an electronic wire etc. has been developed. However, it was what cannot be said to be still enough [this / considering the viewpoint of the practicality as an optical wire, a molecule wire, etc.].

[0005] In order to solve said problem, this invention person has proposed the technique of the condensed ring porphyrin compound which carried out porphyrin ring association and has been prolonged in the one direction used as the base of this invention in which porphyrin rings adjoin each other by three association (three association) with two beta-beta carbon to carbon bonds which two carbon like beta of the next door of the carbon like a mezzo-soprano-mezzo-soprano carbon to carbon bond and said mezzo-soprano combines mutually (application for patent No. 110157 [2000 to]). However, it was what cannot be said to be enough [the number of the porphyrin rings which can condense the ring].

[0006]

[Problem(s) to be Solved by the Invention] The technical problem of this invention develops the structure which raises the die length of delocalization of the expanded pi electron network and an electron, and is to offer the porphyrin compound derivative molecule which approached the utilization as an optical wire, an electronic wire, etc. further by this. Although it is important to stop a HOMO-LUMO gap small when the application as an electronic wire is considered, the porphyrin array which for that conjugate extended more is required, and the porphyrin array which condensed the ring more is considered as a leading candidate compound. Then, this invention technical problem has the structure which condensed the ring more, and is to establish the efficient synthesis method of a porphyrin array with which the HOMO-LUMO gap fell. While considering the synthetic approach of said derivative, to the system of reaction which advances a reaction that said technical problem should be solved An oxidizer, Among the reaction solvent which made the Lewis acid which contains rare earth elements in a compound with the oxidizer chosen [especially] from quinones live together, especially

as a reaction solvent It discovered that the compound which said this invention to which the condensed ring of a porphyrin ring progressed more than invention proposed previously makes a technical problem was obtained by setting up the reaction condition which carries out heating reflux further using what is chosen from aromatic compounds, such as toluene and a benzonitrile. Furthermore, even if it used compounds other than the raw material proposed by previous application, it discovered that the porphyrin compound derivative which condensed the ring by said association of three is obtained, and that reaction effectiveness increased by advancing the porphyrin compound derivative which condensed the ring by association of three proposed previously under said reaction condition, and the technical problem of said this invention was solved. [0007]

[Means for Solving the Problem] The porphyrin ring of the 1st of this invention expressed with said general formula 1 is the condensed ring porphyrin polymer which coupled at least the beta directly with the beta by three covalent bond like a beta with two betas by which at least mezzo-soprano adjoins this with mezzo-soprano. desirable -- said general formula 1 -- setting -- R1 and R -- 4, R10, R13, R16, and R22 it chooses independently of the phenyl group which has the substituent chosen independently of a phenyl group, a with a carbon numbers of one or more alkyl group, or an alkoxy group -- having -- R7 and R19 Independently, respectively Hydrogen, a halogen, a hydroxyl group, a sulfhydryl group, the amino group, The alkyl group which is not permuted [a nitro group, a cyano group, a carboxyl group, a sulfonic group a permutation, or], The alkoxy group which is not permuted [the aryl group which is not permuted / a permutation or /, a permutation, or], The alkylthio group which is not permuted [the aryloxy group which is not permuted / a permutation or /, a permutation, or], The arylamino radical which is not permuted [the aryl thio radical which is not permuted / a permutation or / an alkylamino radical, a permutation, or], The carboxylic-acid amide group which is not permuted [the carboxylate radical which is not permuted / a permutation or /, a permutation, or], The sulfonamide radical which is not permuted [the sulfonate radical which is not permuted / a permutation or /, a permutation, or], It is said condensed ring porphyrin compound characterized by being the siloxy radical which is not permuted [the silyl radical which is not permuted / the carbonyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or]. It sets to said general formula 1 more preferably. R1, R4, R10, R13, R16, and R22 It is said each condensed ring porphyrin compound characterized by being chosen independently of 3, 5-G TASHARU buthylphenyl radical or 3, and 5-G octyloxy phenyl group.
[0008] The porphyrin ring which Zn-porphyrin of said general formula 2 is made to condense the ring in the solvent with which the quinone and rare-earth-elements **** Lewis acid which are an oxidizer exist, and adjoins each other combines the 2nd of this invention mutually with the carbon like each mezzo-soprano. In said said general formula 1 to which the porphyrin ring which adjoins each other by a total of three association of two beta-beta carbon to carbon bonds by the carbon like two beta by which at least the mezzo-soprano adjoins carbon joining together mutually has extended in the one direction n And 0 or one or more integers, The condensed ring metal free porphyrin compound or condensed ring M+n-porphyrin compound (however) to which coordination of demetallization or other metals was carried out for Zn of the condensed ring ZnII-

porphyrin compound whose M is that of Zn, and this condensed ring ZnII-porphyrin compound M is a metal chosen from the group of said metal atoms other than Zn, and n is the manufacture approach of an ionic valence which each metal can take. It sets to a general formula 2 preferably. R1, R4, R7, R10, R13, R16, R19, and R22 A phenyl group, Or the condensed ring ZnII-porphyrin compound according to claim 4 characterized by being the phenyl group permuted by the substituent chosen independently of a with a carbon numbers of one or more alkyl group or an alkoxy group, And the condensed ring metal free porphyrin compound or condensed ring M+n-PO n-porphyrin compound to which coordination of demetallization or other metals was carried out for Zn of this condensed ring ZnII-porphyrin compound (-- however, M is a metal chosen from the group of said metal atoms other than Zn, and n is the manufacture approach of ****** ionic valence) of each metal.

[0009] Make the 3rd of this invention condense the ring in the solvent with which the Lewis acid containing the quinone and rare earth elements which are oxidizers about the ZnII-porphyrin of said general formula 3 exists, and two porphyrin rings combine it mutually with the carbon like each mezzo-soprano. By and a total of three association of two beta-beta carbon to carbon bonds by the carbon like two beta by which at least the mezzo-soprano adjoins carbon joining together mutually The condensed ring metal free porphyrin compound or condensed ring M+n-porphyrin compound to which coordination of demetallization or other metals was carried out for Zn of the condensed ring ZnII-porphyrin compound which condensed the ring, and this condensed ring ZnII-porphyrin compound It is the manufacture approach of (the ionic valence [however,] to which M is a metal chosen from the group of the aforementioned metal atoms other than Zn, and each metal can take n). R1, R3, R4, R6, R7, R9-R12 of said general formula 3 preferably Hydrogen, R2, R5, and R8 Phenyl group, Or said two porphyrin rings characterized by using the ZnII-porphyrin which is the phenyl group which has the substituent chosen independently of a with a carbon numbers of one or more alkyl group or an alkoxy group join together mutually with the carbon like each mezzo-soprano. By and a total of three association of two beta-beta carbon to carbon bonds by the carbon like two beta by which at least the mezzo-soprano adjoins carbon joining together mutually The condensed ring metal free porphyrin compound to which coordination of demetallization or other metals was carried out for Zn of the condensed ring ZnII-porphyrin compound with which the adjacent porphyrin ring is prolonged in the one direction, and this condensed ring ZnII-porphyrin compound, or a condensed ring M+n-porphyrin compound (however) M is a metal chosen from the group of said metal atoms other than Zn, and n is the manufacture approach of an ionic valence which each metal can take.

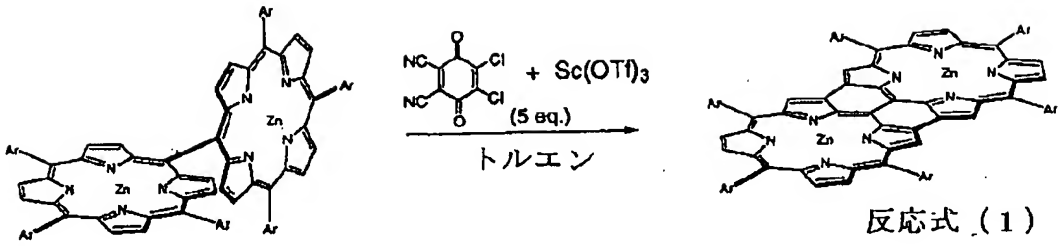
[0010] It sets to invention of each of said manufacture approach more preferably. The condensed ring ZnII-porphyrin compound characterized for using a compound with the phenyl group which permuted TASHARU butyl or an OKUCHIRUOKI radical by the 3 or 5th place as a phenyl group permuted by the substituent chosen independently of a with a carbon numbers of one or more alkyl group or an alkoxy group by things, The condensed ring metal free porphyrin compound or condensed ring M+n-porphyrin compound to which coordination of demetallization or other metals was carried out for this Zn It is the manufacture approach of (the ionic valence [however,] to which M is a metal chosen from the group of the aforementioned metal atoms other than Zn, and each metal can take n). Much more preferably In invention of each of said manufacture

approach The chemical reaction which obtains the compound with which the porphyrin ring which adjoins each other by three association with two beta-beta carbon to carbon bonds which the carbon like two beta next to the carbon like the mezzo-soprano-mezzo-soprano carbon to carbon bond which a porphyrin ring combines mutually with the carbon like each mezzo-soprano, and said mezzo-soprano combines mutually condensed the ring The aromatic hydrocarbon solvent with which the Lewis acid containing the element of the oxidizer chosen from quinones and rare earth exists is used. The condensed ring metal free porphyrin compound according to claim 4 to 8 or condensed ring M+n-porphyrin compound characterized by making it go on under reflux It is the manufacture approach of (the ionic valence [however,] to which M is a metal chosen from the group of the aforementioned metal atom, and each metal can take n).
[0011]

[The mode of operation of this invention] This invention is explained more to a detail.
A. A well-known thing can be used as a compound of the MEZOMEZO joint porphyrin array expressed with said general formula 2 used for manufacturing the compound of this invention. Furthermore, about the compound with which the MEZOMEZO joint porphyrin array developed into 9 or more ****s, this invention person has already proposed (Japanese Patent Application No. No. 248756 [11 to]), and these compounds can also be used as a manufacture raw material of the compound of this invention. Moreover, if the reaction condition using the Lewis acid which contains rare earth elements as an acid catalyst is used, using a quinone compound as an oxidizer of this invention, the condensed ring porphyrin compound derivative combined by three association of said MEZOMEZO association and two beta-beta association is compoundable from the compound expressed with a general formula 3.
[0012] B. The synthetic approach using the compound of the manufacture approach 1. aforementioned general formula 2 of the compound of this invention.
Two beta-beta association at least whose two beta by which at least the mezzo-soprano of the compound of a general formula 2 adjoins (No. 24 [one to] is set lawfully and the location of 5, 10, 15, and 20 is said) combined carbon of each other (1 setting No. -24 lawfully location of 2, 3, 7, 8, 12, 13, 17, and 18) is formed of effective oxidation denaturation. In case a porphyrin array is manufactured, by the way, the 5 and 15-diaryl METARO porphyrins which are [each other] crowded in configuration MEZOMEZO single bond JIPORUFIRIN is compoundable from JIPORUFIRIN (II), for example, Zn, coupled directly and Mg(II) porphyrins. From nickel (II), Cu (II), and Pd (II) porphyrin Single bond mezzo-soprano-beta JIPORUFIRIN is compoundable. And if it oxidizes in nickel (II) and Pd(II) porphyrins with a stronger oxidizing agent [Tori (BUROMO phenyl) ammonium hexa chloro antimonate (BAHA:(p-BrC6H4)3NSbCl6)], mezzo-soprano-beta condensed ring porphyrins are compoundable. Different regioselective (regioselectvity) coupling in said preparation, i.e., MEZOMEZO, and MEZO beta can be explained in relation to the HOMO orbit which involves. That is, to Mg(II) Zn(II) porphyrins, A1u (A1uHOMO which shows big electron density to beta-pyrrole carbon) corresponds to A2u (A2uHOMO which shows a big consistency to mezzo-soprano carbon), nickel (II), Cu (II), and Pd(II) porphyrins. If these results are taken into consideration, MEZOMEZO joint metal JIPORUFIRIN with A1uHOMO which shows big electron density to beta-pyrrole carbon will think that a coupling reaction will occur

in free beta location in the case of oxidation. This invention adopted raw material MEZOMEZO joint ZnII-porphyrins as the bottom of said inference in consideration of said electron density.
[0013] 2. Oxidation process which forms beta-beta association of carbon like two beta which adjoins mezzo-soprano combined carbon.
While the selectivity of said association improved by combining the Lewis acid which contains quinone compounds and a rare earth metal as an oxidizer, for example, rare earth truffe RATO, (rare earth trifluoro methansulfonic acid) while examining the process for going on this oxidation wholeheartedly, it turned out that the condensed ring porphyrin compound which progressed more is obtained.
1. As quinones, DDQ, para benzoquinone, full ora nil (fluoranil), etc. can be mentioned as a desirable compound.
2. As rare earth, Sc, Y, La, Eu, etc. can be mentioned as a desirable thing.
3. As a solvent, toluene, a benzonitrile, etc. which are aromatic hydrocarbon can mention as a desirable thing.
4. As for a reaction, it is desirable to carry out under the reflux in the boiling point of said solvent.
[0014] C. The synthetic approach of the compound of said general formula 3.
1. The conditions of the oxidizer and Lewis acid which are a fundamental reaction condition, and a solvent do not change.
2. Preferably, the quinone of about 5 equivalence is used for an oxidizer forming one duplex condensed ring, and Lewis acid is used on condition that a quinone and equivalence.
[0015]

[Example] A MEZOMEZO joint ZnII-JIPORUFIRIN compound (18mg, 8 mmol) is dissolved in 30ml toluene using the round-head bottle mold flask of example 150mL. Dichloro dicyano paraben ZOKINON DDQ (mg [9], 40mmol) and scandium trifluoro methansulfonic acid Sc (CF3SO3)3 (mg [20], 40mmol) which are an oxidizing agent are added, and a mixed solution is agitated under 1-hour reflux. This mixture is diluted with a methanol and a tetrahydrofuran (THF). A solvent is removed by the rotary evaporator, a product is melted to THF, and it lets it pass to an alumina column. And the condensed ring porphyrin derivative (a duplex condensed ring porphyrin dimer may be called) which is combined with the carbon like beta which adjoins MEZOMEZO association which is made to recrystallize in benzene/acetonitrile and two porphyrin rings combine with the carbon like mezzo-soprano, and this MEZOMEZO association and which is combined by a total of three association of two beta-beta association was obtained (12.9mg, 86%). Said reaction is shown in a reaction formula (1). (A 3 and 5-t-buthylphenyl radical is shown by the inside Ar of reaction-formula (1).)
[0016]
[Formula 4]



反応式（1）

[0017] NMR:1H NMR (CDCl3) 1.41 (s, 36H, t-Bu), 1.45 (s, 72H, t-Bu) 7.35 (s, 4H, Por-b), 7.59 (t, J= 1.8Hz, 2H, Ar-H) 7.61 (t, J= 1.8Hz, 4H, Ar-H), 7.63 (d, J= 1.8Hz, 4H, Ar-H) 7.67 (d, J= 1.8Hz, 8H, Ar-H), 7.70 (d, J= 4.9Hz, 4H, Por-b), and calculated-value =1867;UV/Vis(CHCl3):lambdamax= to 7.75(d, J= 4.9Hz, 4H, Por-b);MALDI-TOF MS m/z=1868 and C124H138N8Zn2 -- 419 (Soret) and 582 (Soret) -- And although it 1068nm. Is the example of manufacture of the duplex condensed ring porphyrin to which application of said point used the CuII-JIPORUFIRIN compound for connecting, yield is a maximum of 82%.

[0018] In the thing of an example 1, the product at the time of changing a reaction solvent, reaction time (reflux time amount), an oxidizer (concentration), and Lewis acid (concentration) and the recovery of a raw material were summarized in Table 1.

[0019]

[Table 1]

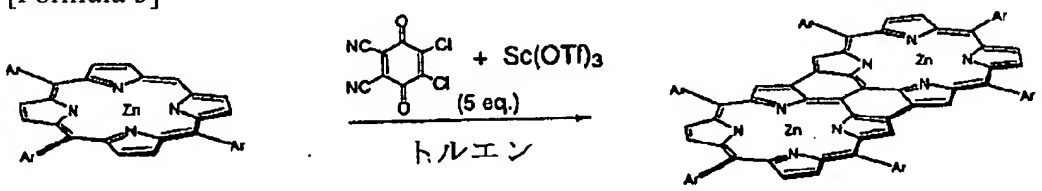
Zn^{II}-二重縮合ジポルフィリンの合成

番号	溶 媒	時間(h)	キノン	当量	ルイス酸	当量	収率(%)	
							2	1(回収)
1	トルエン	0.5	DDQ	5	$Sc(OTf)_3$	5	86	0
2	トルエン	1	DDQ	2.2	$Sc(OTf)_3$	2.2	87	10
3	トルエン	12	DDQ	5	$Y(OTf)_3$	5	20	68
4	トルエン	24	DDQ	5	$La(OTf)_3$	5	16	80
5	トルエン	24	DDQ	5	$Eu(OTf)_3$	5	9	75
6	トルエン	36	DDQ	5	$Mg(OTf)_3$	5	0	74
7	トルエン	20	p-ベンゾキノン	5	$Sc(OTf)_3$	5	56	20
8	トルエン	20	フルオラニル	5	$Sc(OTf)_3$	5	67	27
9	THF	10	DDQ	5	$Sc(OTf)_3$	5	0	96
10	ベンゾニトリル	0.5	DDQ	5	$Sc(OTf)_3$	5	35	0
11	トルエン	20	DDQ	5	—	—	0	80
12	トルエン	20	—	—	$Sc(OTf)_3$	5	0	96

[0020] It is clear from the result of Table 1 that a reaction solvent, reaction time (reflux time amount), an oxidizer (concentration), and Lewis acid (concentration) have brought about the significant operation effectiveness in composition of the porphyrin derivative compound of this invention. Moreover, the results of an example 1 are the compound compounds mono dispersion object [molecule length was equal to in this oxidation-ring closure reaction (duplex condensed ring formation reaction). also about such a mono dispersion compound, this invention person can apply to the polymer (oligomer is included) MEZOMEZO joint porphyrin arrays of] already proposed (Japanese Patent Application No. No. 248756 [11 to]) -- it is ******(ing).

[0021] Example 250mL A MEZOMEZO joint ZnII-hexa porphyrin compound (30mg, 4.7 mmol) is dissolved in 50ml toluene using a round-head bottle mold flask. Dichloro dicyano paraben ZOKINON DDQ (mg [27], 119 mmol) which is an oxidizing agent

Scandium trifluoro methansulfonic acid Sc (CF3SO3)3 (mg [59], 119mmol) is added, and a mixed solution is agitated under 2-hour reflux. They are a methanol and a tetrahydrofuran about this mixture. (THF) It dilutes. A solvent is removed by the rotary evaporator, a product is melted to THF, and it lets it pass to an alumina column. And the condensed ring porphyrin derivative (a duplex condensed ring porphyrin hexamer may be called) which is combined with the carbon like beta which adjoins MEZOMEZO association which is made to recrystallize in benzene/acetonitrile and six porphyrin rings combine with the carbon like mezzo-soprano, and this MEZOMEZO association and which is combined by a total of three association of two beta-beta association was obtained (18.5 mg, 62%).
UV-vis(CHCl3):lambdamax= -- 448 (Soret), 876 (Soret), and 1892nm [0022] The ZnII-porphyrin (30mg, 32mmol) by which the carbon like the mezzo-soprano of examples 35, 10, and 20 is permuted by the phenyl group permuted by the 3 or 5th place by t-butyl is used. In the toluene in which DDQ (36mg, 160mmol) and scandium trifluoro methansulfonic acid Sc (CF3SO3)3 (mg [79], 160mmol) exist By three association with two beta-beta carbon to carbon bonds which the carbon like two beta next to the carbon like the mezzo-soprano-mezzo-soprano carbon to carbon bond which carry out heating reflux, said porphyrin is made to condense the ring, and two porphyrin rings combine mutually with the carbon like each mezzo-soprano, and said mezzo-soprano combines mutually the synthetic approach of the united condensed ring ZnII-porphyrin compound -- it carried out. Yield of 27mg, 90% of yield. The above-mentioned synthetic reaction is expressed with a reaction formula (2). (A 3 and 5-t-buthylphenyl radical is shown by the inside Ar of reaction-formula (2).)
[0023]
[Formula 5]



反応式（２）

[0024] The absorption spectrum to the compound (octamer) with which eight porphyrin rings currently compounded by the approach of this invention condensed the ring is shown in drawing 1 . It is shown that the molecule with which the maximum of the longest absorption wavelength spread to 2600-2700cm-1 is compoundable.
[0025] Q-band of the max of a ZnII-JIPORUFIRIN compound by which the red shift was carried out is observed by 1068nm, and 1 electronic oxidation potential of a MEZOMEZO joint Zn-II JIPORUFIRIN compound decreases to 0.11V with a ZnII-JIPORUFIRIN compound. Therefore, the shift of the potential in a Zn-II complex is more large, and this has suggested the bigger electronic interaction into duplex condensed ring Zn-II JIPORUFIRIN. A tale requires extremely the thing with the duplex condensed ring porphyrin coordination train quite promising in respect of the use as an element of an electronic molecule wire currently proved by low 1 electronic oxidation potential and the increment absorption band which carried out the red shift considerably from a strong electronic interaction. It can expect that such effectiveness improves further in the

porphyrin derivative of this invention which progressed more. The attempt which depends for the electronic interaction of duplex condensed ring JIPORUFIRIN also on a central metal and which this introduces various metals into a JIPORUFIRIN ligand, and is seen is very interesting.
[0026]

[Effect of the Invention] As stated above, the outstanding effectiveness currently proved by 1 electronic oxidation potential with the low compound guided from the porphyrin compound of this invention and the increment absorption band which carried out the red shift considerably that a triple bond porphyrin coordination train is quite promising in respect of the use as an element of an electronic molecule wire is extremely brought about from a strong electronic interaction.

[Brief Description of the Drawings]
[Drawing 1] The absorption spectrum of the condensed ring (octamer) porphyrin compound to which the porphyrin ring extended to eight in the one direction by three

association obtained by this invention